

Service Life Prediction Challenging the Status Quo

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Chapter 6

Highly Predictive Accelerated Weathering of Engineering Thermoplastics

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Investigation of the effect of environmental variables on the degradation of engineering thermoplastics has led to development of accelerated weathering conditions that are highly predictive of changes in gloss and color observed after outdoor weathering in Miami, FL. This can be accomplished in a standard Atlas Ci4000 Xenon arc Weather-Ometer. We have found that using CIRA (IR-reflecting quartz) inner filters and soda lime outer filters on the Xenon arc lamp, a more rain-like water spray, and occasional manual sponge wiping of the samples gives improved results. For 117 samples with 2+ years of Florida weathering data encompassing many types of engineering thermoplastics, the data for gloss loss and color shift have a correlation factor of 3100 ± 680 $\text{kJ/m}^2/\text{nm}$ at 340 nm per year in Miami at the 95% confidence level with generally good fits to the Florida data. The acceleration factor is $7.6\times$. By contrast, at the 95% confidence level, standard SAE J1960 and ASTM G 155 Cycle 1 (formerly G 26 A) conditions had correlations of 1650 ± 1500 and 2000 ± 1300 $\text{kJ/m}^2/\text{nm}$ at 340 nm per year in Miami, respectively. The large variability in these correlation factors due to differences in resin type and pigmentation make these test conditions nonpredictive for engineering thermoplastics.

INTRODUCTION

Rationale and Program

Much effort and expense is put into the accelerated weathering of plastics and other materials for the purposes of optimizing stabilizer formulations, ranking performance, and meeting customer specifications. We assume that accelerated laboratory weathering is somehow predictive of outdoor performance, but often this is not the case. Some practitioners suggest that accelerated weathering tests at best are useful only for ranking materials,¹ but ultimately, manufacturers need to know how long materials will last to make appropriate choices. Often, desired performance is expressed as survival for a certain period at a standard exposure site such as Miami, FL. The goal of accelerated weathering then is to reproduce or predict weathering at that particular standard site.^{2,3} This approach is valid only if weathering in Florida (or elsewhere) is reproducible enough to serve as a benchmark, other regions of the world relate in some way to that site, and accelerated testing can predict performance for new materials.

An important consideration is that weatherability is not an inherent material property; it is a system property. That is, a particular material might weather poorly or well depending on the property being evaluated and on how it is stabilized, pigmented, blended, or textured. For example, a sample might have outstanding color retention, but lose gloss rapidly. If gloss retention is not important for a particular application, then that material weathers well. Some formulations might do very well in black, where color shifts are hidden, but very poorly in white. An otherwise excellent formulation might weather poorly if the colorants are not stable. Since pure polymers are almost never used in any real application, the entire system must be tested, and the evaluation must be predictive.

In 1999 we initiated an effort to accurately predict the weathering of engineering thermoplastics based on aromatic polymers such as BPA polycarbonate, acrylonitrile-styrene copolymers, polyesters, and the like. We were acquiring considerable outdoor weathering data on a wide variety of fully formulated commercial samples as well as simpler model formulations, and we had a quantity of retained samples for accelerated experiments. Our program had several goals: (1) to understand the reproducibility of Florida data as a benchmark; (2) to understand the relationship of other global sites to Florida; (3) to understand the effect of environmental variables on a variety of materials; and (4) to develop laboratory weathering conditions predictive of the Florida benchmark, including an estimate of the statistical certainty of the predictions. In this report we will very briefly describe our results for the first three goals and discuss the fourth in detail. Preliminary reports have already been published,^{4,5} and we intend to publish full papers on all aspects in the near future.

Assumptions for Accelerated Weathering

We believed that a good accelerated weathering test should meet several criteria. First, the light source must be right. By this, we mean that the spectral distribution should match sunlight as closely as possible. Many studies have shown that radiation with wavelengths < 300 nm, which occurs very little in nature, can unnaturally accelerate some polymers and coatings. Bisphenol A polycarbonate, the most widely used polymer in engineering thermoplastics and blends, is a well-known example of a polymer showing such sensitivity to UV radiation with wavelengths < 300 nm.⁶ Gerlock et al. have recently described a coating that also exhibits changes in chemistry with very subtle differences in the light source.⁷ Colorants can degrade from visible light, making the balance of UV and visible important for accurate predictions when both resin and colorants may degrade.

Second, one year's worth of photons in the lab should cause one year's worth of outdoor weathering. If it causes more or less, then the mechanisms of degradation must have been changed, and predictability will be poor. The mechanism change could be due to any of a large number of variables and interactions, but if the relationship between photons absorbed and degradation produced is not

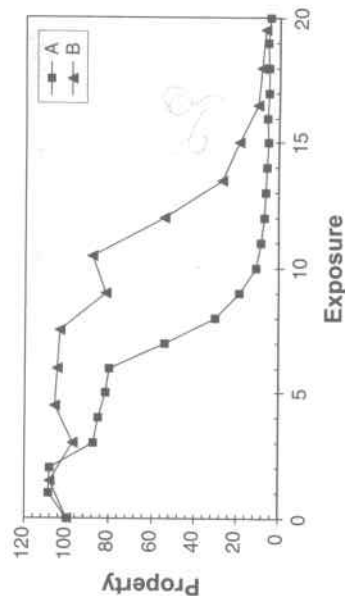


Figure 1a—Hypothetical sets of weathering data.

matched, then the chemistry must have been changed. Since the spectral power distribution of any practical artificial source does not match outdoor sunlight exactly, the dose required to match one year cannot be accurately calculated and any artificial weathering can be only approximate. However, we can assume that for a filtered Xenon arc source, roughly 3500 kJ/m²/nm at 340 nm should give a light dose equivalent to one year in Florida based on the spectral distribution of average Florida sunlight, the annual broadband UV dose in Florida, and the spectral output of filtered Xenon arc lamps.

Third, any accelerated test must by definition increase the rate at which light is applied to the samples. It must be shown experimentally that the material response is linear when increasing the light intensity and/or decreasing the dark periods; that is, the material must show reciprocity. In addition, the variables of temperature and moisture must be properly accounted for in the test procedure.

Fourth, the test must be shown to give the same acceleration for a wide variety of materials. Testing is most useful on experimental, untried materials and formulations for which little or no outdoor data are yet available. One wants confidence that the test is meaningful for many materials at some statistical confidence level. Ad hoc correlations are not useful.

Finally, a test should run on the existing equipment base and not require techniques beyond the reach of reasonably skilled technicians if it is to gain acceptance. Specialized experiments are appropriate for research, but ultimately, procedures must be put into the hands of people doing routine testing.

Treatment of Data

Much weathering data is gathered in tables of property changes after particular exposure periods. While this makes comparisons among samples easy, it is the least informative and least robust way to treat weathering data. One does not know the rate of property change at that point—has it leveled off, or is it deteriorating rapidly? Single points are susceptible to considerable experimental error—was this an outlier, or within the noise of the measurement? We are most interested in questions of rate: how long will something last; how rapidly does the property change; how much longer will it last in region A compared to site B? Tables of data usually do not adequately answer these questions.

Degradation data often are nonlinear and noisy, making it difficult to define a rate constant. A robust way of determining relative rates by the use of shift factors has been described by Simms and others⁸⁻¹⁰ as shown in Figure 1. All of the X values of a data set are multiplied by a factor so that the data points superpose on a reference curve. In Figure 1b, set B superposes on reference set A if the X values are all multiplied by 0.60. If the superposition is good, then the relative rate is this shift factor. If no superposition is possible, then it is not possible to define relative rates. The eye is very good

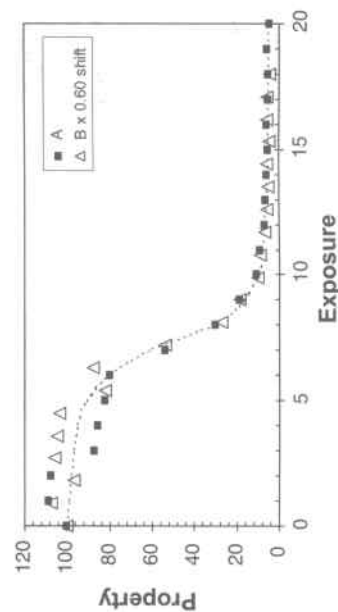


Figure 1b—Data from Figure 1a with the abscissa of set B shifted by a factor of 0.6. The superposition is good.

at determining superposition, and it is usually possible to set up spreadsheets to make this fast and easy. This method is especially robust because it makes use of most of the data points. Determining arbitrary failure times, at 50% property retention for example, emphasizes the importance of the two points nearest the failure criterion and ignores the rest. Any error in these points makes the results more uncertain. All of the relative rates in this work were determined in this way: selection of a reference data set and finding shift factors to superpose the other data sets on the reference. These shift factors are the relative rates.

EXPERIMENTAL METHODS

Samples included BPA polycarbonate (PC), poly(butylene terephthalate) (PBT), acrylonitrile-styrene-butadiene copolymer (ABS), acrylonitrile-styrene-butyl acrylate copolymer (ASA), several developmental polymers, and various blends of these components. Full commercial formulations in several colors as well as simple formulations pigmented with coated rutile TiO_2 or carbon black were tested. We evaluated a set of approximately 110 samples for which good Miami data and unexposed retained samples were available. The measured properties were 60° gloss (using a BYK-Gardner micro TRI glossmeter) and color shift ($\Delta E = (\Delta L^*2 + \Delta a^*2 + \Delta b^*2)^{0.5}$ or yellowness index according to ASTM D 1925 using a GretagMacbeth 7000A colorimeter).

Samples were cut down to 0.5×1.25 in. and attached to 2.625×6 in. aluminum panels using silicone RTV adhesive to form arrays of 24 samples per panel. This allowed efficient use of retained samples and rapid collection of data without sacrifice of accuracy or precision. The arrays were placed backwards in standard Xenon arc sample holders and hung on the inside of the rings in the sample chambers of Atlas Weather-Ometers®. Exposure conditions are shown in Table 1. (The ASTM G 26A standard has been superseded by ASTM G 155 Cycle 1). The SAE J1960 and ASTM G 26A tests were run by Brian Keir of GE Plastics, Selkirk, NY. Outdoor exposures were unbacked, 45° south-facing at the Atlas South Florida Test Service Miami site or other global sites as described in the Discussion section.

Water spray was applied using a special nozzle provided by Atlas: VeeJet model H1/8VV11004 (Spraying Systems Co., Wheaton, IL). This provides a flat spray of 0.28

Table 1—Weathering Exposure Conditions

	SAE J 1960	ASTM G 26A	New GE
Instrument	Atlas Ci65A	Atlas Ci65A	Atlas Ci4000
Inner filter	quartz	boro	CIRA ^b
Outer filter	boro	boro	soda lime
Wavelength cutoff (nm)	270	285	295
Irrad. ($\text{W}/\text{m}^2/\text{nm}$ @ 340 nm)	0.55	0.35	0.75
Air temp (°C)	~50	~45	35
Black panel temp (°C)	70	63	55
Relative humidity (%)	50	50	30
Cycle:			
Light (min)	100 ^a	102	continuous
Light/mist (min)	20 ^a	18	—
Dark (min)	60 ^a	—	—
Dark/rain spray (min)	—	—	30 min once per week
Sponge wipe	—	—	biweekly

(a) Cycle is 40 light / 20 light+mist / 60 light / 60 dark.

(b) IR-reflecting quartz filter from Atlas.

gal/min at 20 psi using at least 2 MΩ deionized/reverse osmosis water. This seemed to give a spray somewhat like rain. However, we found that some samples, particularly ones pigmented with carbon black, did not lose gloss properly even with our best water sprays. An occasional wipe with a sponge and deionized water was required. We gave four double wipes using moderate pressure every two weeks.

Data Analysis

Data were entered into an Excel™ spreadsheet, and Xenon arc and Florida data were plotted on the same graph. Factors corresponding to $\text{kJ}/\text{m}^2/\text{nm}$ at 340 nm per year were applied to the Miami data by trial and error until the Xenon arc and Miami data points gave best superposition as judged by eye. Repeated attempts gave very similar results, and we were unable to devise an analytical fit that did better than the eye. The shift factor becomes the correlation between the accelerated data and Miami. Samples that showed little property change, highly erratic Miami data, or complete change to steady state at the first checkpoint were not included in the analysis.

RESULTS AND DISCUSSION

Reproducibility of Florida Data

Weathering is caused by many factors, but should be driven primarily by sunlight, heat, and moisture. The inherent variability in weather has caused some to question the value of outdoor exposures.¹¹ Much of polymer degradation is driven by highly variable UVB radiation (295–320 nm), but little compiled, long-term data are available for UVB. Records of UV and visible light dosages throughout the spectrum are now being acquired at standard test sites, but such data extend back only a few years while measures of broadband UVA + UVB doses have been regularly measured and published for some time. We have analyzed data from monthly weather summaries issued by the Atlas South Florida Test Service in Miami, FL for the period of 1989 to 2002 and determined the means and standard deviations of the total UV dose (TUV, 295–385 nm) for exposures of various lengths throughout this period. These were calculated with and without assuming an activation energy of 7 kcal/mol to account for temperature effects. The results are shown in Table 2 for the UV dose alone and in Table 3 for the temperature-weighted UV dose. The tables show that exposures <1 year have considerable variability, but that variability drops to about 12% at the 95% confidence level (± 2 standard deviations, $\pm 2\sigma$) at one year and to 6–8% after two years. Temperature variability does not cause much difference for exposures of one year or more. Wet time and relative humidity are relatively constant from year to year, but rainfall is very highly variable. We therefore expect that weathering rates should be generally reproducible within about 10% for exposures of >1 year unless data are taken very close to a time when a property is changing rapidly.

Table 2—Average Cumulative UV Dose (MJ/m^2 295–385 nm; 45° S) at Miami for Various Exposure Periods During 1989–2002

Months	1	3	6	9	12	18	24	30	36	48	60
Dose (MJ/m^2)	23.8	71.5	142.9	214.1	285.2	421.7	571.9	716.3	861.1	1148.9	1435.5
Std dev	3.7	9.2	14.2	16.2	16.9	28.6	19.0	19.7	16.5	18.8	19.3
Std dev (%)	15.6	12.9	9.9	7.6	5.9	6.8	3.3	2.8	1.9	1.6	1.3

Table 3—Average Cumulative UV Dose (MJ/m^2 295–385 nm; 45°S) at Miami for Various Exposure Periods During 1994–2002 Weighted Using an Activation Energy of 7 kcal/mol and the Average High Black Panel Temperatures for Each Month

Months	1	3	6	9	12	18	24	30	36	48
Dose (MJ/m^2)	23.8	71.9	143.9	216.3	288.7	434.6	579.7	727.0	872.6	1019.2
Std dev	4.9	11.1	16.3	17.2	17.8	23.7	22.5	24.7	21.9	23.3
Std dev (%)	20.6	15.4	11.3	8.0	6.2	5.4	3.9	3.4	2.5	2.3

An example of a sample showing such abrupt changes is in Figures 2 and 3. Polycarbonate samples containing 2 or 3% coated rutile TiO_2 pigment were exposed several times at the Miami site. While the data generally define single curves for gloss loss and yellowing, the value at any particular time can vary considerably. It is therefore important to consider the data in its totality. This is especially difficult as the data are coming in slowly point-by-point, but it is the only robust way to look at the data. Surprisingly, replotting the data using MJ/m^2 of UV exposure instead of months as the abscissa did not seem to improve the fit. Other samples for which we have multiple exposures show generally the same results, and will be described elsewhere.

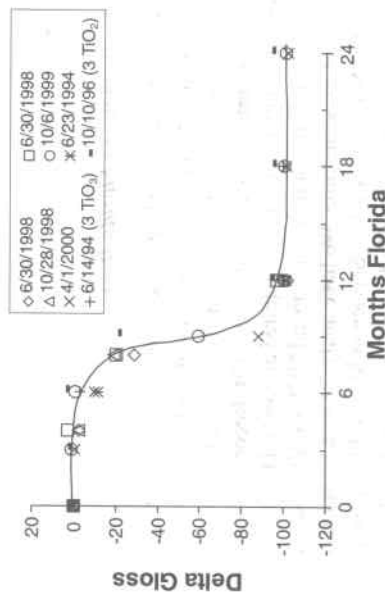


Figure 2—Gloss loss for white PC exposed at various start dates in Miami.

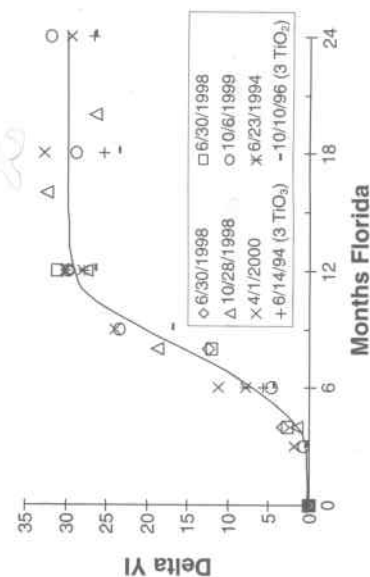


Figure 3—Yellowing of white PC exposed at various start dates in Miami.

times is shown in Figure 4. One sees a great deal of scatter for the three and six month points, as expected, but fairly consistent results for exposures of 12 months and more. The distribution of all the differences among the 228 pairs of readings in Figure 5 show that about 75% were within 10 gloss units and only 10% varied by 20 units or more. The distribution was about the same even when samples showing very little gloss change (< 10 units) were excluded. Similar plots for color shift are shown in Figures 6 and 7. The color shifts seem to show more consistency, with some scatter at all checkpoints. The distribution of the differences among the 228 pairs of readings showed that approximately 80% were within a ΔE of 2 and only 5% were different by 4 or more. Again, the distribution did not change much when samples with $\Delta E < 1$ were excluded.

We conclude that Miami outdoor weathering data can be used as a useful benchmark providing that undue weight is not given to data with < 12 months of exposure and that the total curve is considered. This reduces the noise, and provides much more robust information.

Relationship of Global Sites and Florida Data

We have exposed sets of assorted engineering thermoplastic samples at eight sites worldwide for up to three years and compared the rates of color shift and gloss loss to the set exposed in Miami. Table 4 shows that the relative severity of the sites correlates very well with the relative annual UV doses. Including a temperature term did not improve the correlation. There was considerable variability among the samples used in the experiment with standard deviations 10 to 20% of the means. Thus, the predictability of weathering performance for any particular engineering thermoplastic at any particular site based on Miami data has considerable uncertainty. We will publish full details elsewhere.

Effect of Environmental Variables

LIGHT: Effects of the spectral distribution of the light in the form of activation spectra have been published for many polymers. We have found that the CIRA/soda lime filter combination on Xenon arc lamps gives approximately the same acceleration factor for all aromatic engineering thermoplastics.⁴ To test the effect of light intensity, we exposed resins pigmented with coated rutile TiO_2 behind a series of neutral den-

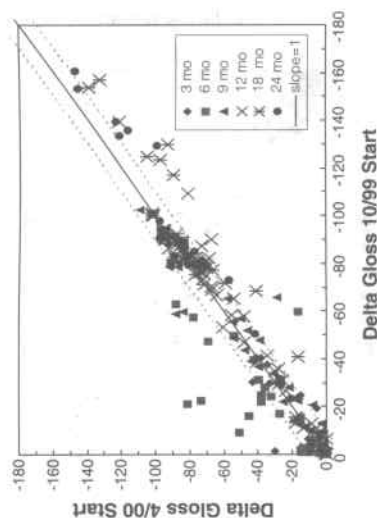


Figure 4—Gloss loss at various checkpoints for samples exposed in Miami starting in October 1999 and April 2000. Dashed lines are at ± 10 units.

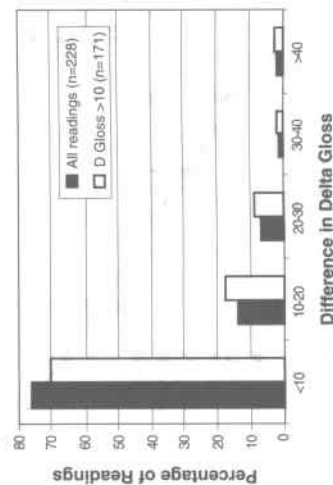


Figure 5—Distribution of differences in gloss loss readings for samples exposed for equal periods in Miami starting in October 1999 and April 2000.

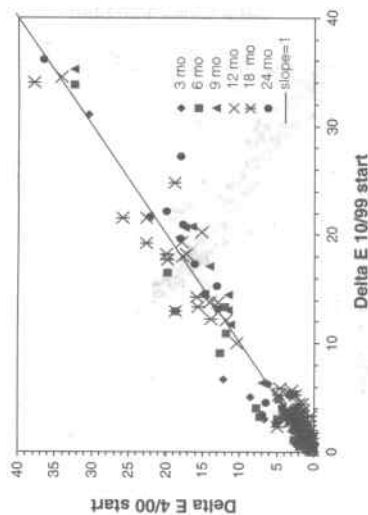


Figure 6—Color shifts at various checkpoints for samples exposed in Miami starting in October 1999 and April 2000.

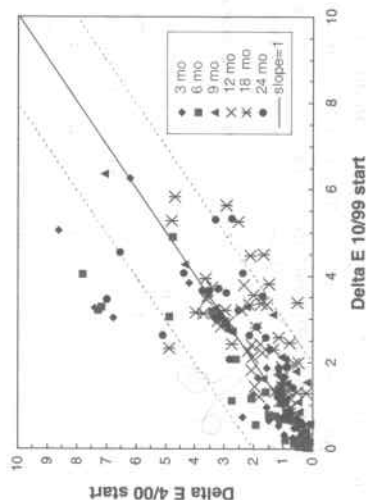


Figure 7—Expanded region of Figure 6. The dotted lines are offset ± 2 units from slope = 1.

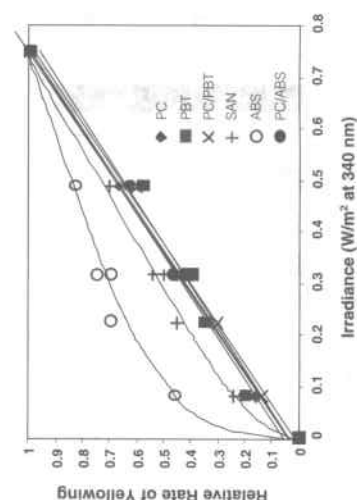


Figure 8—Rates of yellowing of TiO_2 pigmented resins exposed behind neutral density filters using a borosilicate filtered Xenon arc. All relative to rate at $0.75 \text{ W/m}^2/\text{nm}$.

sity filters using borosilicate/borosilicate Xenon arc as the light source. The results in Figure 8 show that the yellowing of PC, PBT, SAN, and various blends all have good reciprocity with light intensity up to an irradiance of at least $0.75 \text{ W/m}^2/\text{nm}$ at 340 nm while ABS does not.⁴ We have found no effect of dark cycles other than that expected from reducing light intensity.

TEMPERATURE: We exposed arrays of samples heated to four different temperatures in Xenon arc Weather-Ometers and determined the activation energies for color shifts and gloss loss. The results are shown in Table 5. The values generally are small and range from 0 to 7 kcal/mol depending on the polymer, property being measured, and exposure conditions. The values indicate that temperature is an important, but not overwhelming, variable except possibly for ABS and other polybutadiene-containing polymers and blends. We conclude that the temperatures of the accelerated test should be as close as possible to those encountered outdoors for good simulation.

MOISTURE: We found that humidity had no effect on gloss loss or color shift for these resins. An experiment in which a simulated acid rain spray was applied weekly also showed very little effect. However, the spray and washing protocol made a very large difference in gloss retention. The spray nozzles standard in the Weather-Ometers apply a very fine mist that does not fully remove degraded polymer and pigment particles from the surface. Its effect is more like dew than rain. Carbon black, especially, builds up to make a velvety surface that is not observed on outdoor samples. We found that

Table 4—Harshness of Global Sites Relative to Miami for Gloss Loss (29 Samples) and Color Shift (14 Samples)

	Niskayuna NY	Phoenix AZ	Louisville KY	Bandol France	Hoek v. Holland	Lochem Holland	Melbourne Australia
Relative UV dose ^a	0.74	1.14	0.81	0.87	0.56	0.54	0.96
Mean relative rates ^b	0.64	1.13	0.81	0.88	0.64	0.61	0.97
Std dev	0.08	0.13	0.09	0.12	0.13	0.14	0.13

(a) Calculated assuming UV at $45^\circ = 4.2\%$ horizontal global except for measured values at Miami and Phoenix.

(b) Average of shift factors necessary to best superpose onto Miami weathering data.

more aggressive sprays improved the appearance somewhat, but still did not accurately reproduce Florida weathering. However, washing the samples with a sponge and deionized water once every week or two produced excellent results. Interestingly, very similar gloss loss is observed for aromatic engineering thermoplastic samples exposed in Arizona and Florida, indicating that even a small amount of natural rainfall is sufficient to drive erosion and gloss loss for these materials.

Improved Exposure Conditions

Our work on the effects of environmental variables led us to the exposure conditions shown in Table 1 as "New GE." The CIRA/soda lime filtered Xenon arc gave the best fit to sunlight using readily available filters, especially at the critical lowest wavelength end of the spectrum as shown in Figure 9. We tried to maintain the lowest air and black panel temperatures possible while setting the irradiance as high as practical. Since there seemed to be no benefit to a dark cycle, we eliminated it. Frequent misting spray cycles caused debris buildup on the samples, so this was replaced by a more aggressive weekly spray and a biweekly sponge wipe (four double strokes with moderate pressure) with deionized water before taking data.

To test the predictability of these conditions, we made arrays of 120 samples, including duplicates, of 117 samples for which we had at least two years of Florida data. The samples represented a wide variety of commercial and developmental engineering thermoplastics in many colors. These were exposed under the new conditions as well as under standard SAE

Table 5—Activation Energies (kcal/mol) and R^2 for Xenon Arc Exposure

Sample	Boro/Boro			CIRA/Soda Lime				
	ΔGloss		ΔYI	ΔGloss		ΔYI		
	E _a	R ²		E _a	R ²			
PBT 3% TiO ₂	3	0.97	3	0.99	2	0.94	4	0.98
PC 3% TiO ₂	3	0.95	4	0.97	4	0.96	5	0.97
PC 0.6% carbon black.....	2	0.92			4	0.97		
PC/PBT blend 3% TiO ₂	1	0.91	4	0.99	3	0.91	5	0.96
PC/PBT blend 0.6% carbon black.....	0				2	0.92		
SAN 3% TiO ₂	3	0.99	4	0.99	4	0.91	5	0.97
ABS 3% TiO ₂	3	0.99	5	0.99	4	0.96	7	0.94
ABS, black								
commercial grade.....	4	0.92			5	0.96		
PC/ABS 3% TiO ₂	3	0.99	5	0.96	4	0.90	7	0.97
ASA 3% TiO ₂	2	0.96	3	0.97	5	0.98	4	0.96

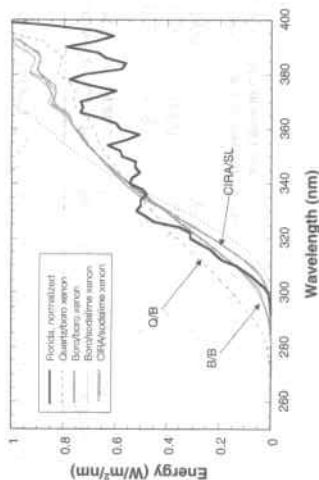


Figure 9—Spectral distribution of light sources.
Source: Atlas Material Testing Technologies, LLC,
Chicago, IL.

The results of this massive experiment are shown in Table 6. The means show the average of all 117 samples for both gloss retention and color shift (ΔE). The standard deviations do not represent the reproducibility of any particular sample, but rather the variability of the correlation factor among different kinds of samples. One sees that the mean correlation factors for J1960 and G 26A are considerably less than the expected $\sim 3500 \text{ kJ/m}^2/\text{nm}$ at 340 nm per year in Florida. In addition, the extreme variability from sample to sample gives J1960 no predictive value at the 95% confidence level. ASTM G 26A is a little better, but still not very predictable. Both did a moderate job at predicting the shape of the degradation curves. By contrast, the new GE conditions had a mean correlation factor of $3100 \text{ kJ/m}^2/\text{nm}$ at 340 nm per year in Florida, well within the expected range. The standard deviation was approximately 10% of the mean giving error bars of approx. 20% at the 95% confidence level. Given that most of these samples showed considerable degradation within 12 months of exposure, and that Florida is reproducible only to within about 10% for one-year exposures, this amount of variability is not bad. In addition, the shapes of the curves were well reproduced in over 90% of the samples.

We attempted to decrease the variability by breaking out samples by resin type, expecting that those containing BPA polycarbonate might be accelerated disproportionately under J1960 and G 26A. This turned out not to be the case for either gloss retention or color shift as shown in Tables 6 and 7. The effect of pigments, especially TiO_2 (whites) and carbon black, caused great variability even within resin types. Also note that superposition was not possible (rating = 0) for a significant number of samples under the standard protocols while the new conditions gave some indication of Florida performance for nearly all samples. We conclude that the standard testing protocols have little predictive value for aromatic engineering thermoplastics.

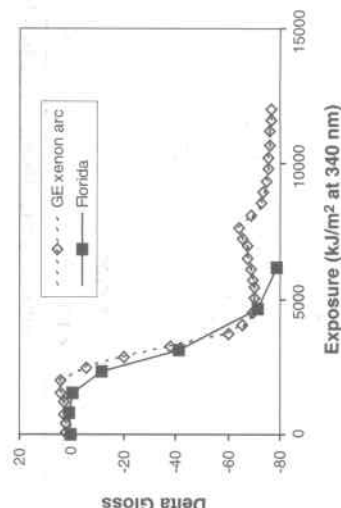


Figure 10—Superposition of Miami data on Xenon arc data for a sample of white ASA/PC blend using a shift factor of $3100 \text{ kJ/m}^2/\text{nm}$ (340 nm) per year of Miami exposure.

Table 6—Correlation of Xenon Arc to Florida for the Set of 117 Samples

Conditions	Mean	Std. Dev. (% of mean)	Florida Correlation ($\text{kJ/m}^2/\text{nm}/\text{year}$ at 340 nm)	Quality of Fit (Scale 0-3)	% of Samples ≥ 2
SAE J1960 (gloss)	1500	700 (47%)	700 (47%)		72%
SAE J1960 (color)	1800	860 (46%)	860 (46%)		72%
ASTM G 26 (gloss)	1900	680 (36%)	680 (36%)		78%
ASTM G 26 (color)	2100	670 (32%)	670 (32%)		78%
New GE (gloss)	3100	340 (11%)	340 (11%)		92%
New GE (color)	3100	340 (11%)	340 (11%)		92%

Reproducibility and robustness of the new GE conditions can be judged in Figure 11 for polycarbonate pigmented with carbon black—a particularly difficult sample. These experiments had variations in spray and wiping procedures to test the robustness of the conditions. One sees generally good reproduction of the Florida data. By contrast, the G 26 and J1960 conditions predict rapid total gloss loss and fail to predict the extended plateau period that we repeatedly found in outdoor weathered samples. Figure 12 shows similar results with a black commercial ABS resin, another difficult sample. (Samples with TiO_2 rather than carbon black pigments had much better reproducibility.) Figure 13 shows both color shift and gloss loss for an experimental resin containing blue colorants. Both the resin and colorants of this sample underwent color shifts. The new GE conditions gave a good indication of Florida weathering while G 26 and J1960 accelerated gloss loss and color shift differently—causing much faster changes in gloss loss than in color shift. The Florida gloss loss for this sample showed a considerable decrease at the first checkpoint, and later it recovered. This point was taken after a particularly dry period with smoke from neighboring forest fires forming deposits not removed by the normal gentle wash procedure. The rainy summer period that followed

Table 7—Correlation of Xenon Arc to Florida Gloss Loss for the Set of 117 Samples Broken Out by Resin Type

Resin Class	Florida Correlation (kJ/m ² /nm/year at 340 nm)		"New GE"
	J1960	G 26	
PC mean (n=10)..... std. dev.	1390 600	1520 730	3100 320
PC/PBT blends..... mean (n=34)..... std. dev.	1500 770	1920 720	3000
PC/other blends mean (n=25)..... std. dev.	1360 720	1810 730	3230 533
Others mean (n=48)..... std. dev.	1490 650	1880 610	3130 300
Overall..... mean (n=117)..... std. dev. (% of mean)	1500 700 (47%)	1850 680 (37%)	3100 240 (11%)
Failed to fit*	14%	7%	1%

(a) Data did not superpose even vaguely on Florida data.

(a) Data did not superpose even vaguely on Florida data.

Table 8—Correlation of Xenon Arc to Florida Color Shift for the Set of 117 Samples Broken Out by Resin Type

Resin Class	Florida Correlation (kJ/m ² /nm/year at 340 nm)		"New GE"	
	J1960	G 26	J1960	G 26
PC (n=10)	mean	1600	1190	3100
	std. dev.	1100	1076	330
PC/PBT blends (n=34)	mean	1810	1670	3000
	std. dev.	820	740	0
PC/other blends (n=25)	mean	2020	1240	3120
	std. dev.	760	630	355
Others (n=48)	mean	2440	2150	3100
	std. dev.	700	790	345
Overall (n=117)	mean	2100	1800	3100
	std. dev.	670	860	240
	(% of mean)	(32%)	(46%)	(11%)
Failed to fit ^a	18%	0%	23%	

(a) Data did not superpose even vaguely on Florida data.

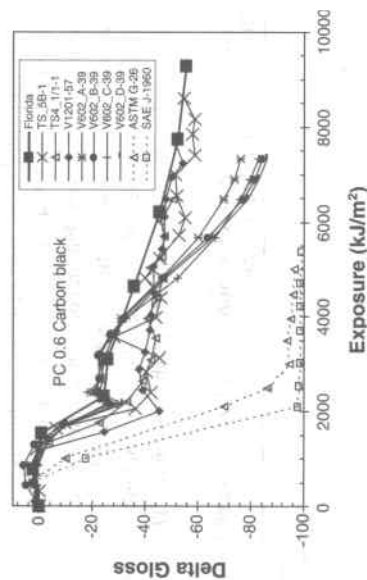


Figure 11—PC containing carbon black tested repeatedly under new GE conditions, G 26, J1960, and Florida (with correlation factor of 1 year = 3100 kJ/m²/nm at 340 nm).

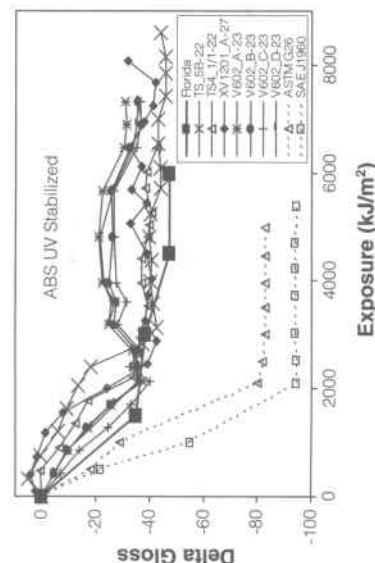


Figure 12—ABS containing carbon black tested repeatedly under new GE conditions, G 26, J1960, and Florida (with correlation factor of 1 year = 3100 kJ/m²/nm at 340 nm).

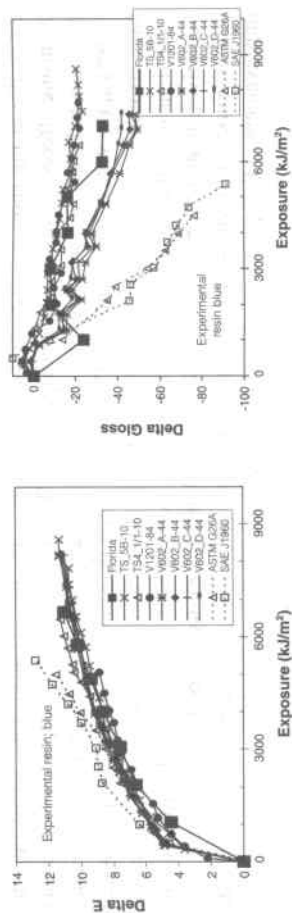


Figure 13—Color shift and gloss loss for a blue experimental resin tested repeatedly under new GE conditions, G 26, J1960, and Florida (with correlation factor of 1 year = 3100 kJ/m²/nm at 340 nm). Both colorant and resin undergo a color shift.

washed away these deposits and restored the gloss. This is a good illustration of the kind of noise sometimes encountered in outdoor data, and the need to evaluate the data in total.

We have restricted our studies to only appearance properties, and do not know whether or not changes in mechanical properties are predicted under these exposure conditions. Testing mechanical properties requires large numbers of fairly large samples, so this kind of study involving > 100 formulations probably is not practical.

Extension to Other Materials

In many ways, the group of aromatic engineering thermoplastics is an easy case because they degrade rather reproducibly. Most of the degradation usually is confined within about 50 microns of the surface, making oxygen diffusion relatively unimportant. In addition, additives and products do not diffuse significantly in the glassy polymers. Polyolefins have the opposite characteristics; they seem highly variable because impurities drive initiation reactions, and diffusion of oxygen and small molecules are both important. This may cause rates of polyolefin photodegradation to be nonlinear with increasing light intensity due to diffusion-limited processes, thus making acceleration of any kind problematic. To our knowledge, no studies on polyolefins over a range of light intensities have been published. Until such work is undertaken, we cannot know if we can expect predictive weathering of polyolefins under any conditions.

We are now studying a few coatings under our new conditions, but lack the wide range of samples that is required to develop confidence in the results. Gerlock found that our conditions did not adequately reproduce the degradation of one of his very sensitive coatings⁷ probably due to imperfect simulation of Florida sunlight. In addition, wet times and humidity are likely to play a more important role in coating weathering than they did for these materials, while coatings probably are less sensitive to the type of spray and any wiping procedures. A study similar to this one using 100 different coating formulations quite possibly would optimize on other exposure conditions. In all cases, we would benefit from a light source that more closely simulates sunlight.

CONCLUSIONS

Our studies find Florida weathering to be an adequate benchmark as long as one considers many data points and exposures periods > 1 year. Keys to good accelerated weathering of aromatic engineering thermoplastics are: (1) light with spectral distribution matching sunlight,

especially at the short wavelength end of the spectrum, and (2) adequately simulating the cleansing effects of rainfall (and perhaps wind). We have shown that it is possible to predict Florida weathering performance for a wide variety of samples with error bars of approximately 20% at the 95% confidence level. This is much better than industry standard conditions that have error bars of 60–100% at the 95% confidence level. While far from perfect, these new conditions have the advantage of working on the existing equipment base and not being particularly difficult to run. At least one commercial test laboratory has begun to use these conditions. Further refinement would require a light source that better matches sunlight and some improvement in the spraying and washing procedures.

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